A Structurally Characterised Pair of Dicobalt(III) Peroxo/Superoxo Complexes with C_2-Symmetrical Tetrapodal Pentadentate Amine Ligands, and Some Reactivity en route

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Dedicated to Professor Martin A. Bennett on the occasion of his retirement

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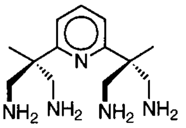
The tetrapodal pentaamine ligand 2,6-bis(1′,3′-diamino-2′-methylprop-2′yl)pyridine (pyN_4, **1**) provides square-pyramidal coordinated cobalt(II) building blocks, which have been used in the synthesis of the singly-bridged dicobalt(III) μ_2-η^1:η^1-peroxo and superoxo complexes $[(\mathbf{1})Co–O_2–Co(\mathbf{1})]^{4+/5+}$, isolated as the chloride, bromide, and mixed chloride/dithionate and bromide/dithionate salts. The peroxo complex is accessible by the classical route involving oxygenation of $[(pyN_4)Co^{II}]$, but has also been obtained from a cobalt(III) precursor in air, which implies that the pentaamine **1** acts as a multi-electron reductant. Oxidation of the peroxo complex with chlorine generated in situ from an HCl/H_2O_2 mixture (H_2O_2 derived from partial peroxo complex hydrolysis) generates the superoxo complex. Both cations have highly symmetrical solid state structures, locked in transoid Co–O–O–Co conformations by two pairs of intramolecular hydrogen bonds. Each involves two protons in the equatorial $Co(NH_2R)_4$ plane of one half of the molecule and the bridge oxygen atom in the other half. A significant difference between the two structures is the orientation of the O_2 bridge, which is coplanar with the pyridine rings of the coordination caps in the peroxo complex and at right angles in the superoxo complex. The reactivities of the complexes in acidic and basic media have been explored, and the mononuclear bromo complex $[(\mathbf{1})CoBr]^{2+}$ was isolated in one of the products. Dithionite, intended as an external reducing agent in the reaction of $Na_3[Co^{III}(CO_3)_3]$ with **1**, instead yields the *S*-sulfito complex cation $[(\mathbf{1})Co(SO_3)]^+$, by disproportionation of $S_2O_4^{2-}$ to give SO_3^{2-} and S^{2-}. All complexes have been characterised by ^1H, ^{13}C NMR, IR, Raman, UV/Vis, and EPR spectroscopy (as applicable), elemental analysis and X-ray structure determination, and the cyclic voltammetry parameters of the peroxo/superoxo pair of complexes have been determined.

Introduction

With a view to creating an active ligand periphery for octahedrally coordinating transition metal ions, we recently introduced a tetrapodal pentadentate amine ligand with an NN_4 donor set (pyN_4, **1**).[1] This ligand acts as a highly symmetrical square-pyramidal coordination cap,[2] and derivatisation of the equatorial NH_2 groups[3] is aimed at creating a functional environment for a monodentate "substrate" at the sixth coordination site. Judicious choice of functional groups should allow for the fine-tuning of secondary interactions between the substrate and the ligand periphery (such as hydrogen bonding, interaction with an electrochemically active centre, π,π-stacking, etc.) and thus enable the modulation of substrate reactivity.[4] An alternative approach is to link pyN_4 coordination caps through suitable bridges so as to create polynucleating ligands,[5] which can bind two or more metal centres having "labile" coordination sites in close proximity.



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Mononuclear cobalt(III) complexes of the parent ligand **1** that have been isolated so far have a chloro,[1] an OH,[6] or a CH_3[7] ligand at the sixth coordination site. The kinetic inertness and the known reactivity of Co^{III} amine complexes with respect to Mannich-type transformations of the coordinated ligands[8,9] led us to further explore this class of complexes. Dinuclear complexes with a suitable bridge linking two $[M(pyN_4)]^{n+}$ fragments have two adjacent $M(H_2NR)_4$ planes, which opens up the possibility of connecting the two coordination caps. In the case of M = Co, a readily introduced bridge can be derived from dioxygen.

Peroxo and superoxo amine complexes of cobalt(III) have been the subject of scientific investigations for at least 150 years,[10–12] the first detailed study being that of Frémy in 1852. He noted that aqueous ammonia solutions containing cobalt(II) salts turn dark upon exposure to air. He isolated

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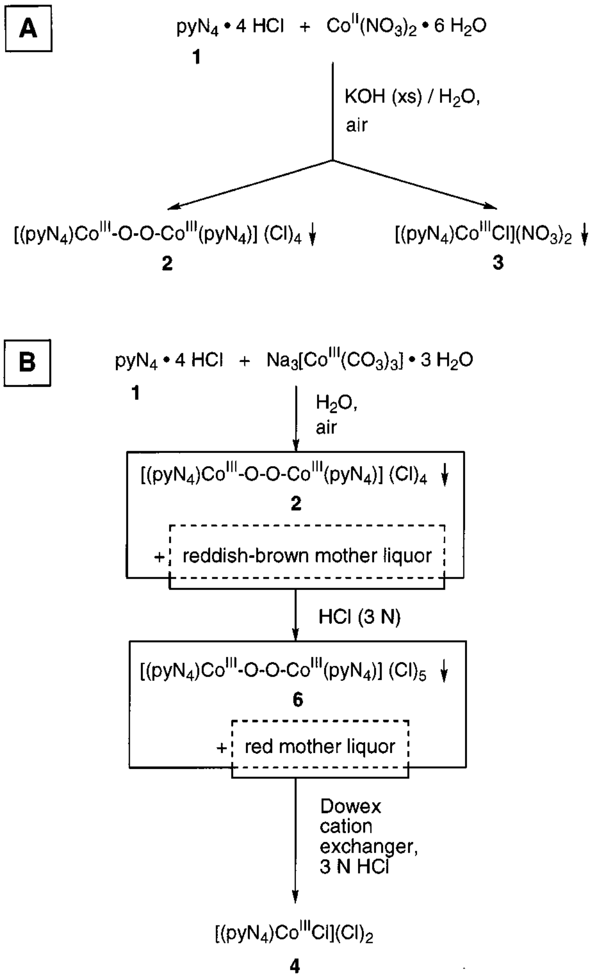
and analysed the brown compound $[Co_2(NH_3)_{10}O_2](SO_4)_2 \cdot 3H_2O$ and found that it evolved oxygen when redissolved in water.[13,14] Work by Maquenne and Vortmann followed, recording facile oxidation of the brown material, which led to a "class of dark green compounds".[15,16] Werner and Mylius were the first in 1898 to describe the brown products as ammine complexes containing two cobalt atoms linked by an O_2 bridge, $[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5]^{4+}$ $(X^-)_4$, and to assign the general formula $[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5]^{5+}$ $(X^-)_5$ to the green products.[17] Both assignments were confirmed after structural techniques became available.

Structural analogues of these prototypes with chelating amine ligands were subsequently prepared. The potential of these and similar complexes as oxygen carriers for a variety of applications was soon recognized[18–20] and has been actively investigated to this day.[21–23] The literature on singly-bridged dinuclear peroxo and superoxo amine complexes of cobalt(III) is extensive, and the structures of a large number of peroxo complexes have been determined. The structural characterisation of superoxo complexes has, by contrast, been accomplished much less frequently, and there is little precedent in the literature where the parameters of singly-bridged peroxo and superoxo cobalt(III) complexes with otherwise identical ligands have been compared.[24–26] For these reasons, we chose to investigate the formation and structure of dinuclear cobalt(III) complexes of **1** with a dioxygen-derived bridging group, as well as some peripheral reactions, and present results in this contribution.

Results and Discussion

Simplicio and Wilkins showed that oxygen uptake by ammoniacal cobalt(II) solutions is due mainly to the reaction of the pentakis(ammine) aqua complex $[Co(NH_3)_5(H_2O)]^{2+}$, whereas the bis(aqua) and tris(aqua) complexes $[Co(NH_3)_4(H_2O)_2]^{2+}$ and $[Co(NH_3)_3(H_2O)_3]^{2+}$ are virtually inert.[27,28] While such species do add oxygen when the nitrogen donor atoms are incorporated into chelate ligands, oxygenation is clearly enhanced as a consequence of an increasing number of ammine or amino groups coordinated to cobalt.[11] A variety of chelating pentaamines, including an early example of a tetrapodal pentadentate ligand,[29,30] have been investigated in this context, and a number of μ-peroxo complexes thus obtained have been structurally characterised. Synthesis usually involves oxygenation of aqueous solutions of cobalt(II) salts in the presence of a ligand.[31–41] As described below, this method was successful with the pentaamine ligand **1**, but we also found an alternative route which uses dioxygen from air, a cobalt(III) starting material, and no apparent reducing agent.

$[(\mathbf{1})Co{-}O{-}O{-}Co(\mathbf{1})]Cl_4$ (2)



Scheme 1. Preparation of dicobalt(III) peroxo and superoxo complexes of the pentaamine ligand **1**

Procedure A: The peroxo-bridged dinuclear tetrachloride **2** was obtained as a brown microcrystalline precipitate from a cooled aerated aqueous solution containing stoichiometric quantities of $\mathbf{1} \cdot 4HCl$[1] and $Co(NO_3)_2 \cdot 6H_2O$ (see Scheme 1, Part **A**). An excess of potassium hydroxide was used to neutralise the acid form of the amine ligand, resulting in a basic reaction medium. No attempt was made to optimise the yield (9%), which may increase with longer reaction times. A significant amount of a red crystalline material identified as $[(\mathbf{1})CoCl](NO_3)_2$ **3**, precipitated from the filtrate upon standing for several days. Compound **2** may be recrystallised from water to give the hydrate $[(\mathbf{1})Co{-}O{-}O{-}Co(\mathbf{1})]Cl_4 \cdot 3H_2O$, as indicated by elemental analysis. Solubility in other polar protic solvents, such as methanol and DMSO, is also high. Contrary to the observations with other dicobalt(III) peroxo complexes,[12] **2** does not release dioxygen upon heating the solid in vacuo (145 °C, 12 h), and the material is recovered unchanged. The IR spectrum of **2** has bands characteristic of the pyN_4 coordination cap. An intense absorption in the Raman spectrum at 800 cm^{-1} is assigned to the O–O stretching vibration, in agreement with data obtained for related complexes.[21,42] Compound **2** is diamagnetic, and its ^1H NMR spectrum ($[D_6]$DMSO, room temp.) resembles that recorded for the mononuclear chloro complex $[(\mathbf{1})CoCl](Cl)(ClO_4) \cdot H_2O$,[1] with two signals of triplet and doublet multiplicity in the intensity ratio 1:2 for the pyridine ring protons. The Co–O–O–Co unit is not expected to be linear. Hence, rotation around the Co−O bond must be fast on the NMR time scale as the spectrum shows all amine and methylene groups to be equivalent. The geminal protons in these groups are, however, diastereotopic, and each gives rise to a set of two well-resolved resonances. The assignment of the exocyclic CH_3 protons is straightforward. The ^{13}C NMR spectrum mirrors the diagnosis of fast rotation of the $\{(pyN_4)Co\}$ fragments in solution, and supports the assumption of highly symmetrical coordination caps. The UV/Vis spectrum of **2** has an intense band at 295 nm. Such a band is due to the $\pi_\sigma^*(O_2^{2-}) \rightarrow d_{z^2}(Co)$ LMCT transition.[43] In solution spectra, it has been suggested to be typical of *trans*-μ_2-η^1:η^1-dicobalt(III) peroxo complexes in which the Co−O−O−Co unit is planar (dihedral angle of 180°).[34,37] Bands at ca. 325 nm and ca. 375 nm, which would indicate a nonplanar arrangement of the Co−O−O−Co unit in solution, are absent.[34,37] However, in the light of our NMR spectral data which imply conformational nonrigidity of the Co−O−O−Co unit in solution, the observed UV/Vis spectrum more likely reflects primarily the symmetrical ligand field of the pyN_4 ligand, whereas a ligand field of lower symmetry is expected to produce a two-band spectrum.[44] The cyclic voltammogram of **2** has a quasi-reversible redox wave associated with the peroxo/superoxo system at $E_{1/2} = +\ 0.40$ V (vs. NHE; solvent: DMSO; for other conditions see Experimental Section).[45] Two irreversible one-electron waves are recorded at $E_{1/2} = -1.11$ V and $E_{1/2} = -1.67$ V, respectively, which we assign to the sequential reduction of the cobalt(III) centres to cobalt(II).[33,36]

Procedure B: We fortuitously found an alternative synthesis of **2** when we wished to repeat the preparation of the mononuclear complex $[(\mathbf{1})CoCl](X)_2$ (X = Cl: **4**). The published procedure[1] requires that all manipulations be carried out under a blanket of dinitrogen, allowing the isolation of red $[(\mathbf{1})CoCl](Cl)_2$ as the primary product. Performing the reaction between $Na_3[Co(CO_3)_3]{\cdot}3H_2O$ and **1**·4HCl in air under otherwise identical conditions (including a water/methanol solvent mixture) gave a brown microcrystalline precipitate which was found to be the dinuclear peroxo-bridged tetrachloride **2** (isolated yield accounts for 18% of **1**; see Scheme 1, Part **B**). The mother liquor was basic. Compound **2** did not precipitate quantitatively, owing to its marked solubility in water. Workup of the mother liquor allowed the sequential isolation of the superoxo complex $[(\mathbf{1})Co{-}O{-}O{-}Co(\mathbf{1})]Cl_5$ **(6)**, and the mononuclear chloro complex $[(\mathbf{1})CoCl](Cl)_2$ **(4)** (see below). The NMR, IR, Raman and UV/Vis spectroscopic data of **2** obtained according to procedure **B** are identical to the data determined for the product prepared by route **A**. Addition of an excess of sodium dithionate to an aqueous solution of **2** gave single crystals of $[(\mathbf{1})Co{-}O{-}O{-}Co(\mathbf{1})](S_2O_6)Cl_2{\cdot}6H_2O$ **(5)** which were suitable for an X-ray structure analysis.

$[(\mathbf{1})Co{-}O{-}O{-}Co(\mathbf{1})]Cl_5$ (6)

In Procedure **B** (see above and Scheme 1, Part **B**), a reddish-brown filtrate remained after the isolation of precipitated peroxo complex **2**, still containing a sizeable amount of this complex in solution. Acidification of this filtrate with hydrochloric acid and reaction overnight produced a green crystalline precipitate and a red solution. The ESR spectrum of the isolated crystalline material (DMSO, 120 K) has a Zeeman splitting factor of $g = 2.0269$, which is in agreement with the formulation of the product as a singly-bridged dicobalt(III) superoxo complex. Hyperfine coupling with the ^{59}Co nucleus is not observed.[26,46] Elemental analysis of a recrystallised sample showed that the product was a bridged superoxo complex $[(\mathbf{1})Co{-}O{-}O{-}Co(\mathbf{1})]Cl_5$, **6** (isolated yield accounts for 14% of **1**). Further support comes from the Raman spectrum of a solid sample (dispersant: KBr) which shows a strong absorption at 1075 cm^{-1}, in a region typical of ν(O−O str) of other bridged superoxo complexes.[21,42] The UV/Vis spectrum has bands of varying intensity at 208, 307, 464, and 698 nm and is thus in good qualitative agreement with the spectrum reported for $[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5]Cl_5{\cdot}4H_2O$.[47] As expected, the cyclic voltammogram of the superoxo complex (determined for the mixed chloride hexafluorophosphate salt $[(\mathbf{1})Co{-}O{-}O{-}Co(\mathbf{1})]Cl_2(PF_6)_3$) corresponds to that of the peroxo complex **2** (above). The red filtrate of this reaction provided, upon workup, the desired mononuclear complex **4** (yield accounts for 19% of **1**). Partial anion exchange of **6** with sodium dithionate gave single crystals of $[(\mathbf{1})Co{-}O{-}O{-}Co(\mathbf{1})](S_2O_6)_2Cl{\cdot}10H_2O$ **(7)**, which were suitable for X-ray structure analysis.

The superoxo complex was also formed when sulfuric acid was used instead of hydrochloric acid for the acidification of the reaction mixture, as long as the reaction was performed on the chloride salt **2**. Alternatively, the superoxo complex formed when the perchlorate salt $[(\mathbf{1})Co{-}O{-}O{-}Co(\mathbf{1})](ClO_4)_4$ was reacted with HCl. The superoxo complex did not form when the perchlorate salt was treated with H_2SO_4. Instead, the colour of the solution turned orange, indicating the formation of a mononuclear species, presumably the aqua complex $[(\mathbf{1})Co(OH_2)]^{3+}$. Aqueous hydrogen peroxide alone showed no reaction with either the chloride or the perchlorate salt. When allowed to react with the chloride salt **2**, a mixture of hydrogen peroxide and hydrochloric acid produced the superoxo complex much faster (as judged by the change of colour from brown to green) than hydrochloric acid alone.

Our conclusions from these observations are as follows: (i) Unlike Procedure **A**, the reduction equivalents required for the generation of the peroxo bridge in Procedure **B** cannot originate from the metal precursor as this already contains cobalt in the +3 oxidation state. Methanol as reductant cannot be excluded at this stage (see, however, below) but we have no indications for the formation of formaldehyde which would be the likely oxidation product. Alternatively, a decomposition pathway may operate by which a certain amount of pentaamine ligand **1** is oxidised, with concomitant formation of cobalt(II), which is subsequently reoxidised upon reaction with aerial dioxygen.[48] This would explain the moderate yields of **2**, **4** and **6** obtained from these reactions (only about 50% of **1** is accounted for in the products); (ii) The chloride ion and water are unlikely reductants for Co^{III}, on the grounds that the redox potentials of the half-reactions $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$ and $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ are too high for Co^{III} to accomplish either oxidation and be reduced in the presence of amine ligand. While experimental evidence indicates that $Na_3[Co(CO_3)_3]\cdot 3H_2O$ reacts with aqueous HCl in the absence of other ligands to form the hexaaqua complex $[Co^{III}(H_2O)_6]^{3+}$ (which is a powerful oxidant in aqueous solution, generating O_2, H^+, and $[Co^{II}(H_2O)_6]^{2+}$), it is unlikely that in the presence of the chelating amine ligand, cobalt(II) can originate from this reaction. We have no experimental data to support the notion that in our system of peroxo and superoxo complexes, the O_2 bridge derives from dioxygen generated internally, by a Co^{III}/Co^{II} redox reaction as indicated above. In the original preparation of the mononuclear chloro complex **6** under an inert atmosphere,[1] formation of the peroxo complex was not observed. Impurities or decomposition products in the starting material, $Na_3[Co(CO_3)_3]\cdot 3H_2O$, might act as a source of cobalt(II), but batches were freshly prepared, and elemental analyses indicated the correct composition; (iii) For the transformation of **2** into **6** upon addition of hydrochloric acid, we postulate HCl-induced decomposition of **2** and liberation of hydrogen peroxide[48] (Equations 1a−c). At a critical HCl concentration, mixtures of H_2O_2 and HCl are known to form Cl_2,[49] which acts as an oxidising agent on the peroxo complex **2** and produces the superoxo complex **6** (Scheme 1, Part **B**). This assumption is supported by the fact that neither hydrogen peroxide alone nor a combination of chloride-free acid and non-halide salt of the peroxo complex will produce the superoxo complex. In a separate experiment, a brown aqueous solution of **2** reacted immediately with gaseous chlorine or its solution in water to give a green precipitate. The formation of cobalt(III) superoxo complexes by reaction of the peroxo complexes with halogens has been described in the literature.[11,26]

$$\underset{\textbf{2}}{[(pyN_4)Co^{III}\text{-O-O-}Co^{III}(pyN_4)](Cl)_4} + 2\ HCl \longrightarrow 2\ [(pyN_4)Co^{III}Cl](Cl)_2 + H_2O_2 \tag{1a}$$

$$H_2O_2 + 2\ HCl \longrightarrow Cl_2 + 2\ H_2O \quad (\text{at critical [HCl]}) \tag{1b}$$

$$2\ \underset{\textbf{2}}{[(pyN_4)Co^{III}\text{-O-O-}Co^{III}(pyN_4)](Cl)_4} + Cl_2 \longrightarrow 2\ \underset{\textbf{4}}{[(pyN_4)Co^{III}\text{-O-O-}Co^{III}(pyN_4)](Cl)_5} \tag{1c}$$

$$3\ [(pyN_4)Co^{III}\text{-O-O-}Co^{III}(pyN_4)](Cl)_4 + 4\ HCl \longrightarrow 2\ [(pyN_4)Co^{III}\text{-O-O-}Co^{III}(pyN_4)](Cl)_5 + 2\ [(pyN_4)Co^{III}Cl](Cl)_2 + 2\ H_2O \tag{1d}$$

$[(\textbf{1})Co{-}O{-}O{-}Co(\textbf{1})]Br_4$ (8) and $[(\textbf{1})Co{-}O{-}O{-}Co(\textbf{1})]Br_5$ (10)

For clarification of the circumstances surrounding the formation of **2** from a cobalt(III) precursor in air, some of the reactions described above were repeated in the absence of methanol with the methanol-free salt $\textbf{1}\cdot 5HBr$, or with the hydrobromide/methanol solvate $\textbf{1}\cdot 4HBr\cdot MeOH$, and with a variation of pH. The methanol-free hydrobromide was prepared from the methanol solvate by ion exchange chromatography (Dowex 50W×2, eluent: 3 N HBr). The reaction of equimolar quantities of $\textbf{1}\cdot 5HBr$ and $Na_3[Co(CO_3)_3]\cdot 3H_2O$ under a blanket of nitrogen in degassed water gave an orange solution, which upon exposure to air, deposited the tetrabromide salt **8** as a greenish-brown crystalline material in an isolated yield accounting for 21% of **1**. The solubility of the tetrabromide **8** in water is far lower than that of the tetrachloride **2**, making precipitation near-quantitative. The mother liquor contained the mononuclear bromo complex $[(\textbf{1})CoBr](Br)_2$ (**9**) as the only other isolated product. Repeating the reaction with $\textbf{1}\cdot 4HBr\cdot MeOH$ and a water/methanol (1:1 v/v) solvent mixture under otherwise identical conditions gave essentially the same results. A further experiment combined $\textbf{1}\cdot 4\ HBr\cdot MeOH$ (10 mmol), $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (10 mmol), and HBr (10 mmol) in a water/methanol solvent mixture, the reaction being carried out in air (see Experimental Section). The tetrakis(hydrobromide) salt provides four equivalents of acid, while sodium tris(carbonato)cobaltate contains six equivalents of base. We reasoned that further addition of acid would make more cobalt(III) available for complexation. After reaction, the mixture was found to be at pH 7, and the peroxo complex **8** was isolated in the highest yield recorded in this series of experiments (accounting for 56% of **1**). Workup of the mother liquor provided the bromo complex **9** in a yield accounting for 22% of **1**. An experiment with additional HBr (pH after the reaction was 4) gave, instead of the peroxo complex, the bromo complex **9** as the exclusive product. Heating an authentic sample of **9** at reflux under a stream of air for an extended period of time (12 h), in the presence or absence of methanol, did not produce the dinuclear peroxo complex; rather, **9** was partially transformed into the aqua complex $[(\textbf{1})Co(H_2O)]Br_3$, as indicated by ^1H NMR and IR spectroscopy.[50] Finally, the superoxo complex **10** was obtained as green microcrystals from a suspension of peroxo complex **8** in 3 N HBr in an isolated yield of 65% relative to **8**. From the mother liquor was isolated the bromo complex **9** as the only other product. The IR, Raman, NMR and UV/Vis spectroscopic parameters of **8** and **10** (as applicable) are similar to those determined for the corresponding chloride salts **2** and **6**. Addition of excess sodium dithionate to an aqueous solution of **8** gave single crystals of $[(\textbf{1})Co{-}O{-}O{-}Co(\textbf{1})](S_2O_6)Br_2\cdot 6H_2O$ (**11**), and partial anion exchange of **9** with NH_4PF_6 (carried out in a similar manner) gave single crystals of $[(\textbf{1})CoBr]Br(PF_6)\cdot H_2O$ (**12**). Both batches of crystals were suitable for X-ray structure analysis.

Our conclusions from the observed reactivity are as follows: (i) Methanol as a possible reductant may be excluded; (ii) The addition of one extra equivalent of acid increases the yield of peroxo complex **8** markedly. Products containing close to 80% of the initially employed pentamine ligand **1** were isolated, making the involvement of **1** as a *one*-electron reductant questionable; (iii) The action of bromide ion as reductant in the formation of the peroxo complex may be excluded since only the aqua complex is generated in a control experiment. Moreover, the generated bromine should induce further oxidation, leading to the superoxo complex, which is not observed; (iv) The yield of superoxo complex from the reaction of the peroxo complex with HBr corresponds exactly to the theoretical value expected on the basis of Equation 1d. This observation suggests that processes analogous to those described by Equations 1a−1c for the chloride salt operate for the bromide salt: the acid-induced decomposition of one third of the peroxo complex yields hydrogen peroxide which oxidises bromide ion to bromine, which in turn oxidises the remaining two thirds of peroxo complex.[11]

Overall, the most likely explanation for the observed reactivity is that the polyamine ligand **1** acts as a multiple-electron donor, depending on the reaction conditions. We are currently seeking to identify a specific ligand oxidation product. An amino acid ester has previously been suggested to be the electron source in the preparation of a bridging peroxo cobalt(III) dimer from a cobalt(III) precursor in air.[48]

The reactivity of the described peroxo and superoxo complexes with varying pH may be summarised as follows: Once generated, the peroxo complexes may be transformed into bridged superoxo and mononuclear species upon addition of a suitable acid. In aqueous alkaline solution (pH ≥ 12), the peroxo complexes are stable for hours without noticeable decomposition, while the superoxo complexes react with aqueous ammonia to reform the peroxo complexes. Similar reactivity has been documented for a number of O_2-bridged dicobalt(III) complexes with other polyamine ligands.[11]

[(**1**)$CoSO_3$]Br (**13**)

With a view to studying the effect of an external reducing agent on the generation of the peroxo complex **8** from $Na_3[Co(CO_3)_3]\cdot 3H_2O$ and **1**$\cdot$4HBr$\cdot$MeOH in air, we reacted two equivalents each of the cobaltate and the pentaamine ligand in the presence of one equivalent of sodium dithionite in water, which contained an excess of $NaHCO_3$ ($Na_2S_2O_4$ has been used to decompose $Co^{II}-O_2$ adducts, but the product(s) deriving from the dithionite ion have never been identified[27]). The only isolated products of this reaction were a finely divided black solid (which tested positive for S^{2-} and is presumably Co_2S_3) and an orange-brown microcrystalline precipitate identified as the *S*-sulfito complex [(**1**)$CoSO_3$]Br (**13**) by elemental and X-ray structural analysis (yield accounts for 39% of the pentaamine ligand **1**). The formation of Co_2S_3 and **13** in the presence of dithionite implies disproportionation of the latter, a reaction known to occur in basic solution,[51] particularly in the presence of heavy metal salts having a propensity to form sulfides (Equation 2). There is no indication of the intermediacy of a cobalt(II) species in the formation of **13**.[52] The observed formation of **13** contrasts with the classical synthesis of cobalt(III) *S*-sulfito amine complexes, in which the SO_3^{2-} ligand is introduced in the form of sodium disulfite ($Na_2S_2O_5$), which hydrolyses rapidly on dissolving in water to give an equilibrium mixture of $SO_2/HSO_3^-/SO_3^{2-}$.[53,54] Cobalt(III) *S*-sulfito amine complexes have been studied in detail because of the particularly strong kinetic and structural *trans* effect exerted by the SO_3^{2-} ligand,[53,55−59] a phenomenon which causes some of the compounds to have unusual catalytic[60] and redox properties.[52,60]

$$3\,S_2O_4^{2-} + 6\,OH^- \longrightarrow 5\,SO_3^{2-} + S^{2-} + 3\,H_2O \qquad (2)$$

Solid State Structures

Structural details of the square-pyramidally coordinated {(pyN_4)Co} fragment have been described elsewhere,[1,6,7] and the corresponding bond lengths and angles in compounds **5**, **7**, **12** and **13** are given in Table 1 for reference. Parameters that quantify distortions (if any) of the ligand cap are listed in Table 2. The structures of **3** and **11** have been determined and deposited with the Cambridge Structural Database but will not be discussed, as their parameters are similar to those of [(**1**)CoCl](Cl)(ClO_4)$\cdot H_2O$[1] and **5**, respectively. The discussion addresses the salient structural features of the cations in **5**, **7**, **12** and **13**, especially the conformation of and intramolecular hydrogen bonding in the O_2-bridged dinuclear complexes.

[(**1**)Co−O−O−Co(**1**)](S_2O_6)$Cl_2\cdot 6H_2O$ (**5**)

The cation (Figure 1) contains two virtually undistorted octahedral cobalt(III) centres and lies on a twofold crystallographic rotation axis which passes through the midpoint of the O−O bond. The 4+ charge on the cation is consistent with the assignment of the bridging group as peroxide, and the Co−O [1.883(3) Å] and O−O bond lengths [1.467(5) Å] as well as the Co−O−O angle [110.7(3)°] are all within the range of values found for other Co(N_5) peroxo complexes.[37] The dihedral angle Co1−O1−O1A−Co1A is 177.5(2)°. The Co−O−O−Co core is virtually coplanar with the pyridine ring N11···C15, the best planes being at an angle of 4.62(3)°. As a consequence of the inherent molecular symmetry, the two CoN_4 units are parallel and adopt an eclipsed conformation with respect to each other (Figure 2a). Relevant nonbonded distances within the (N_4)Co−O−O−Co(N_4) subunit are listed in Table 3. The Co−N bond *trans* to the O_2^{2-} group (1.928(4) Å) is significantly shorter than the equatorial bonds (on average 1.950 Å), both values being similar to the corresponding bond lengths in the pentaamine peroxo complex [(trenen)-Co−O−O−Co(trenen)](ClO_4)$_4$ [trenen = *N*,*N*,*N'*-tris(2-

Table 1. Selected bond lengths [Å] and angles [°] for compounds **5**, **7**, **12** and **13** with estimated standard deviations in parentheses; see also Table 3

Bond or angle	**5**	**7**	**12**	**13**
Co1−N11	1.928(4)	1.928(2)	1.934(5)	1.997(3)
Co1−N12	1.945(3)	1.958(2)	1.964(4)	1.968(4)
Co1−N13	1.950(3)	1.949(2)	−	1.978(4)
Co1−N14	1.950(3)	1.955(2)	−	1.973(4)
Co1−N15	1.956(3)	1.946(2)	1.960(5)	1.968(4)
Co1−X[a]	1.883(3)	1.915(2)	2.422(1)	2.226(1)
N11−Co1−X[a]	177.7(1)	177.11(8)	179.6(2)	179.2(1)
N11−Co1−N12	90.7(1)	91.74(9)	91.2(2)	88.5(2)
N11−Co1−N13	92.4(1)	88.1(1)	−	91.6(1)
N11−Co1−N14	92.2(2)	93.10(9)	−	91.0(1)
N11−Co1−N15	91.2(2)	90.5(1)	90.2(2)	89.7(2)
X−Co1−N12[a]	90.1(1)	89.21(9)	89.0(1)	91.9(1)
X−Co1−N13[a]	89.7(1)	89.18(9)	−	89.1(1)
X−Co1−N14[a]	87.1(1)	85.98(9)	−	88.7(1)
X−Co1−N15[a]	86.7(1)	92.21(9)	89.5(1)	89.6(1)
N12−Co1−N13	88.8(2)	90.6(1)	−	88.4(2)
N12−Co1−N15	91.8(1)	91.8(1)	90.8(2)	90.7(2)
N13−Co1−N14	91.6(1)	90.2(1)	−	92.2(2)
N14−Co1−N15	87.6(2)	87.6(1)	−	88.7(2)
N12−Co1−N12A	−	−	88.2(3)	−
N15−Co1−N15A	−	−	90.2(3)	−
Co1−N11−C11	119.6(3)	119.6(2)	118.8(5)	119.9(3)
Co1−N11−C15	120.3(3)	119.9(2)	119.7(5)	119.7(3)
N11−C11−C18	116.7(4)	117.6(2)	118.6(6)	116.6(3)
N11−C15−C22	116.6(4)	117.0(2)	118.3(6)	116.8(4)
C12−C11−C18	123.0(3)	122.3(2)	121.9(7)	122.5(4)
C14−C15−C22	122.4(4)	122.7(2)	121.8(7)	123.0(4)
C11−C18−C19	112.9(4)	112.9(3)	112.9(6)	111.8(4)
C15−C22−C23	112.7(4)	112.3(2)	111.7(7)	112.2(4)
C11−C18−C16	110.4(4)	106.5(3)	108.8(4)	111.3(4)
C15−C22−C21	109.6(4)	111.0(2)	110.1(4)	109.5(4)
C16−C18−C19	106.5(3)	107.6(3)	107.2(4)	106.8(4)
C21−C22−C23	106.8(4)	107.2(2)	107.1(5)	107.1(4)
C16−C18−C17	111.5(4)	109.6(3)	−	110.5(4)
C16−C18−C16A	−	−	112.0(6)	−
C21−C22−C20	111.6(4)	111.1(2)	−	110.7(4)
C21−C22−C21A	−	−	110.5(7)	−
C18−C16−N12	113.0(3)	111.7(2)	113.8(5)	114.2(4)
C22−C21−N15	113.5(4)	113.3(2)	113.1(5)	114.0(4)
C16−N12−Co1	118.5(3)	118.7(2)	118.6(3)	118.0(3)
C21−N15−Co1	118.4(3)	118.2(2)	118.5(3)	118.7(3)

[a] **5**: X = O1; **7**: X = O1; **12**: X = Br1; **13**: X = S1.

Table 2. Intramolecular angles [°] and distances [Å] quantifying the slight distortions of the ligand cap in complexes **5, 7** and **13** (with estimated standard deviations in parentheses); compound **12** does not show these distortions owing to crystallographically imposed symmetry; see footnote and text for definitions of angles

Bond or angle	**5**	**7**	**13**
ε[a]	4.07(5)	5.5(5)	6.0(5)
ζ[b]	2.5(2)	1.8(2)	4.1(3)
η[c]	2.3(2)	2.9(1)	5.4(2)
d(C16···C21)[d]	5.085(6)	5.019(5)	5.124(7)
d(C17···C20)[d]	4.922(6)	5.017(4)	4.884(7)

[a] Angle ε between the least-squares planes defined by the pyridine ring (N11, C11, C12, C13, C14, C15) and the quaternary and methyl carbon atoms C18/C19/C22/C23. − [b] Angle ζ between the least-squares planes defined by the equatorial nitrogen atoms N12/N13/N14/N15 and the methylene carbon atoms C16/C17/C20/C21. − [c] Angle η subtended by the lines N11···C13 and N11−Co1 at N11. − [d] This distance is 5.032(8) Å in **12**.

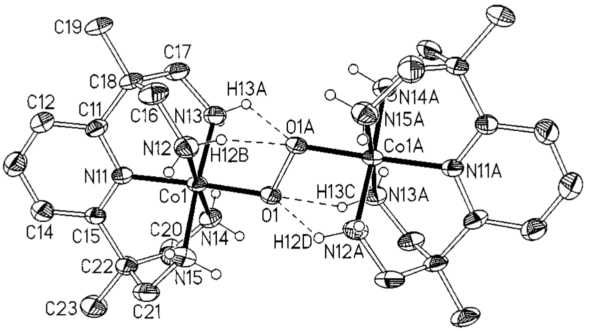


Figure 1. Molecular structure of the peroxo complex cation in **5** with thermal ellipsoids at the 50% probability level; only the hydrogen atoms in the $Co(NH_2R)_4$ planes are shown, and intramolecular hydrogen bonds are indicated by dashed lines

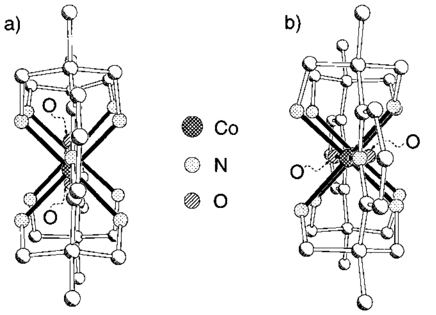


Figure 2. Views along the Co−Co vector of the peroxo (a) and superoxo (b) complex cations in **5** and **7**, respectively, illustrating the eclipsed conformations of the pyN_4 coordination caps; relative to the pyridine rings, the O_2 bridge is coplanar in (a), and positioned at right angles in (b)

Table 3. Characteristic angles (°), bonded and nonbonded distances (Å) within the $(N_4)Co-O-O-Co(N_4)$ subunits of **5** and **7** with estimated standard deviations in parentheses

Angle or distance	**5**	**7**
Co1−O1−O1A−Co1A	177.5(2)	180
Co1−O1−O1A	110.7(3)	116.5(2)
Co1−O1	1.883(3)	1.915(2)
O1−O1A	1.467(5)	1.325(3)
Co1···O1A	2.765(3)	2.771(2)
Co1···Co1A	4.497(2)	4.576(1)
O1···N12	2.709(4)	2.720(3)
O1···N13	2.704(4)	2.712(3)
O1···N14	2.640(5)	2.639(3)
O1···N15	2.635(5)	2.782(3)
O1···N12A	2.767(5)	2.872(3)
O1···N13A	2.747(5)	3.845(3)
O1···N14A	3.846(5)	3.726(3)
O1···N15A	3.851(5)	2.921(3)
N12···N(x)	x = 15A: 4.359(6)	x = 14A: 4.411(4)
N13···N(x)	x = 14A: 4.435(6)	x = 15A: 4.637(4)

aminoethyl)ethane-1,2-diamine][37] and, incidentally, the mononuclear hydroxo species $[(\mathbf{1})Co(OH)](ClO_4)_2$.[6] This contrasts with a marked *trans* influence of the peroxo ligand found in the structures of other CoN_5 complexes, where the Co−N(*trans*) bond can be up to 3% longer than the other Co−N bonds.[37,61]

In the solid state, the central Co−O−O−Co moiety of **5** is locked in a transoid conformation by four intramolecular hydrogen bonds indicated as dashed lines in Figure 1, defining the "triangular" arrangement N12−H12B···O1A···H13A−N13 and its symmetry-related counterpart [averaged distances and angles: d(N···O) = 2.76 Å; (N−H···O) =

126°]. Similar triangular intramolecular hydrogen bonding with planar Co−O−O−Co units has been found in the complexes $[(en)(dien)Co{-}O{-}O{-}Co(dien)(en)](ClO_4)_4$,[62] $[(tren)(NH_3)Co{-}O{-}O{-}Co(NH_3)(tren)](SCN)_4\cdot 2H_2O$[63] and $[(papd)Co{-}O{-}O{-}Co(papd)](S_2O_6)(NO_3)_2\cdot 4H_2O$[34] (papd = 1,5,8,11,15-pentazapentadecane), and the adopted solid state conformations of bis[pentaaminecobalt(III)] peroxo cations have been discussed in terms of the balance of such intramolecular hydrogen-bonding interactions and lattice energy effects.[34] Intramolecular hydrogen bonding which significantly *distorts* the Co−O−O−Co core of a dicobalt(III) peroxo species from planarity has been described for $[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5](SO_4)_2\cdot 4H_2O$,[25] and most recently also for a complex with carbohydrate-derived ligands.[64]

[(**1**)Co−O−O−Co(**1**)]$(S_2O_6)_2Cl\cdot 10H_2O$ (**7**)

Figure 3 shows the molecular structure of the cation, which formally consists of two essentially undistorted octahedral cobalt(III) centres linked by an O_2^- bridge, with an inversion centre at the midpoint of the O−O bond. The superoxo nature of the bridge is evident from the 5+ charge on the cation and the significantly shorter O−O bond length [1.325(3) Å] relative to **5**. This value and the Co−O distance [1.915(2) Å] and Co−O−O angle [116.5(2)°] are similar to the corresponding values determined for other $Co(N_5)$ superoxo complexes.[24,26,36,65] Molecular symmetry requires the Co−O−O−Co unit to be planar and, in the same way as in **5**, implies that the CoN_4 "squares" are parallel and adopt an eclipsed orientation (Figure 2b). It can be seen from Table 3 that, while the metal centres in **7** are further apart than in **5**, the other nonbonded distances within the $(N_4)Co{-}O{-}O{-}Co(N_4)$ framework are similar in both structures. Also, the Co−N bond lengths in **7** are virtually identical to those in **5**. Most significantly, the bond *trans* to the *superoxo* bridge in **7** has the same length (within experimental error) as the bond *trans* to the *peroxo* bridge in **5** and is significantly shorter than the equatorial bonds. In the two previously characterised pairs of cobalt(III) peroxo/superoxo complexes with otherwise identical ligands,[24−26] the $Co{-}N_{trans}$ distance decreased markedly on going from peroxide to superoxide. It should be noted at this point that the coordination geometry imposed by the pyN_4 ligand does not necessarily obscure the *trans*-influence of ligands at the sixth site. A strong *trans*-influence is apparent in the structure of $[(\mathbf{1})Co(CH_3)]S_2O_6$,[7] and still discernible in the structure of **13** (below).

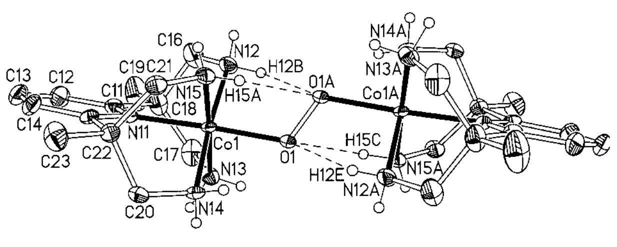


Figure 3. Molecular structure of the superoxo complex cation in **7** with thermal ellipsoids at the 50% probability level; only the hydrogen atoms in the $Co(NH_2R)_4$ planes are shown, and intramolecularhydrogen bonds are indicated by dashed lines

The most striking difference between the structures of **5** and **7** in the solid state is that, while the peroxo group is coplanar with the pyridine rings in **5**, the superoxo group in **7** is orientated at essentially right angles to them [87.0(2)°, which is the angle between the best planes defined by Co−O−O−Co and the pyridine ring N11···C15, respectively). The intramolecular hydrogen-bonding in **7** is again triangular, but this time involves nitrogen atoms on either diaminopropyl sidearm of the pyN_4 coordination cap [N12−H12B···O1A···H15A−N15 and its symmetry equivalent; averaged distances and angles: d(N···O) = 2.90 Å; (N−H···O) = 107°]. It is assumed that the different hydrogen-bonding requirements[26,66] of the bridging groups in either salt, as well as electrostatic effects due to the different sets of counterions, are responsible for the change in the solid state conformation upon oxidation. Density functional theory-based calculations are currently being performed[67] in order to gain insight into the electronic structures of the adopted geometries.[43,65]

[(**1**)CoBr]$Br(PF_6)\cdot H_2O$ (**12**) and [(**1**)$Co(SO_3)]Br\cdot 3H_2O$ (**13**)

The coordination cap of the cation in **12** (Figure 4a) is perfectly regular, owing to a crystallographic mirror plane which contains the pyridine ring. Distances and angles are similar to the values observed for **5** and **7** (Table 1), and also to those of the related chloro complex $[(\mathbf{1})CoCl](Cl)(ClO_4)\cdot H_2O$.[1] The $Co{-}N_{ax}$ bond in **12** is again slightly shorter [1.934(5) Å] than the four $Co{-}N_{eq}$ bonds [1.960(5) and 1.964(4) Å]. The Co−Br bond length at 2.422(1) Å lies in the range of values for this bond in other bromocobalt(III) complexes.[68][69] The molecular structure of the *S*-sulfito complex cation in **13** is shown in Figure 4b. The coordination cap is essentially regular (Table 1). The sulfito ligand shows rotational disorder, which may be a consequence of mismatched intra-cation hydrogen bonding between the protons on the equatorial N_4 donor set and the three trigonally disposed sulfito oxygen atoms. Two preferred orientations of the sixth ligand (with occupancy factors of 75% and 25%) have been refined. The Co−S bond length is 2.226(1) Å and thus ident-

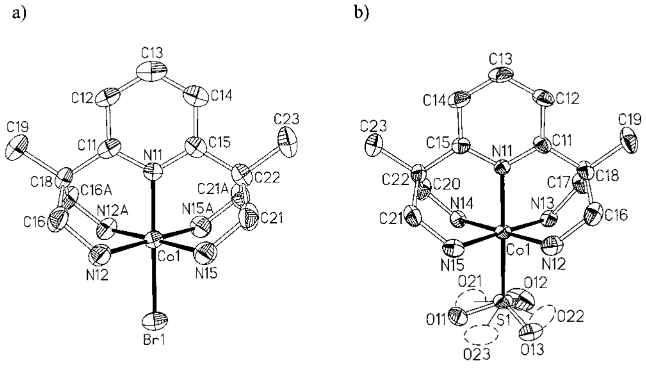


Figure 4. Molecular structures of the mononuclear cations in **12** (a) and **13** (b), with ellipsoids at the 50% probability level; hydrogen atoms have been omitted for clarity; the other resolvable orientation of the *S*-sulfito ligand in **13** is indicated by dashed ellipsoids

ical to the value in the related complex $[(en)_2(NH_3)Co(SO_3)]ClO_4$ [2.227(2) Å].[57] In contrast to the situation in complexes **5**, **7** and **12**, there is a noticeable structural *trans*-influence of the sixth ligand in **13**, as is evident from $Co-N_{ax}$ and $Co-N_{eq}(av)$ bond lengths of 1.997(3) Å and 1.972(4) Å, respectively. This influence of the *S*-sulfito ligand in **13** is, however, not as pronounced as in a *trans*-ammine-bis(ethylenediamine)cobalt complex, where the difference between axial and averaged equatorial bond lengths is 0.11 Å.[57]

Conclusion

The work presented here extends the series of known cobalt(III) complexes of the type $[(\mathbf{1})CoX]^{n+}$, in which the tetrapodal pentaamine ligand **1** acts as a highly symmetrical square pyramidal coordination cap. While the preparation of mononuclear complexes with X = Br^-, H_2O is straightforward, it is unusual for X = SO_3^{2-}, which involves the disproportionation of dithionite ion to SO_3^{2-} and S^{2-}. Singly-bridged dinuclear μ_2-η^1:η^1-peroxo and -superoxo complexes $[(\mathbf{1})Co-O_2-Co(\mathbf{1})]^{4+/5+}$ are accessible by established methods [oxygenation of a cobalt(II) precursor/oxidation of the peroxo complex thus formed]. The peroxo complex may, however, be obtained in a better yield from a cobalt(III) precursor in air, which implicates the pentaamine **1** as a multi-electron reductant under the chosen conditions. The most significant solid-state structural difference between peroxo and superoxo complex is the orientation of the O_2 bridge relative to the pyridine rings of the coordination caps. Both complexes have parallel $Co(NH_2R)_4$ units in an eclipsed conformation on either side of the O_2 bridge. The peroxo complex is stable in basic aqueous solution and thus represents an attractive template for Mannich-type reactions which may, by analogy to the preparation of "sepulchrates" pioneered by Sargeson, lead to molecules with an encapsulated Co−O−O−Co spine. Work to this end is currently in progress.

Experimental Section

Materials and Instrumentation: Manipulations were performed in air unless otherwise stated. Reagents were AR grade or better and were purchased from Merck, Fluka, and Aldrich. Compounds **1**·4HCl[1] and **1**·4HBr·MeOH[70] were prepared as described previously. IR (KBr discs) and UV/Vis spectra (solvent: water) were recorded on Perkin−Elmer 16PC FT-IR and Shimadzu UV-3101 PC instruments, respectively. Cyclic voltammograms were recorded using an EG & G potentiostat PAR model 264A and a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum auxiliary electrode and a platinum reference electrode (scan rate: 20 mV s^{-1}). NMR spectra were measured on a JEOL JNM-EX 270 spectrometer, and mass spectra were obtained on a JEOL MSTATION 700 spectrometer. Elemental analyses were performed using Carlo Erba Elemental Analysers 1106 and 1108. The ESR spectrum (DMSO glass, 120 K) was obtained on a Bruker ESP 300E instrument. Raman spectra were measured with a laser spectrophotometer (Coherent Inova 90) using argon-ion excitation at 514 nm over the region 400−3400 cm^{-1}.

X-ray Crystallography: Crystal data for compounds **5**, **7**, **12** and **13** are given in Table 4, and selected distances and angles are listed in Table 1−3. The structures of the cations are presented in Figure 1, Figure 3, and Figure 4. Data for compounds **3** and **11** have been deposited (CCDC) but are not discussed. All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using either SHELXTL 5.03[71] (**7**, **12**) or SHELXTL 5.1.[72] The hydrogen atoms of **5** and **12** were geometrically positioned and allowed to ride on their carrier atoms during refinement; their isotropic displacement parameters were tied to those of the adjacent atoms by a factor of 1.2 or 1.5. For **7** and **13**, hydrogen atom positions were obtained from a difference Fourier synthesis and refined with a common fixed isotropic displacement parameter. Hydrogen atoms for the solvate water molecules of **5**, **12**, and **13** were not included.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137875 (**3**) − -137880 (**13**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

[(1)Co−O−O−Co(1)]Cl$_4$ (2). − Procedure A: The preparation was carried out in air and essentially followed the procedure given by Mori et al.[73] To a solution of **1**·4HCl (3.00 g, 7.55 mmol) in water (3 mL) was added a solution of KOH (1.70 g, 30.3 mmol) in water (2 mL). This solution was added slowly (pipette) with stirring to a filtered solution of $Co^{II}(NO_3)_2 \cdot 6H_2O$ (2.20 g, 7.55 mmol) in water (5 mL). In the course of the addition, the mixture turned brown, and a turbidity appeared. The mixture was cooled to 5 °C, and reacted with a stream of compressed air from the immersed tip of a Pasteur pipette for 90 min. A solution of $NaNO_3$ (0.88 g, 10 mmol) in water (1.5 mL) was then added, and bubbling of the ice-cooled solution continued for 30 min., after which time a microcrystalline brown precipitate had formed. This was filtered over a glass frit (porosity G4), washed with cold water (2 mL), then with ethanol (3 mL) and diethyl ether (3 mL), and dried in vacuo. After recrystallization from a small amount of warm water (4 mL) the isolated yield of single crystals was 0.56 g (0.71 mmol, 9.3%). The crystals were suitable for X-ray crystallography. − IR (KBr): $\tilde{\nu}$ = 3442 cm^{-1} (s), 3194vs, 2968m, 2934m, 2880w, 1606m, 1468m, 1394m, 1384m, 1167m, 1102m, 1037m, 762m, 560m. − ^1H NMR ([D$_6$]DMSO, room temp.): δ = 8.19 [AB$_2$, 3 lines, ^3J(HH) = 8.07/8.07 Hz, 2 H, H^4], 7.72 [AB$_2$, 2 lines, ^3J(HH) = 8.07 Hz, 4 H, H^{3,5}], 5.47 [br. m, 8 H, −N*H*H−], 5.27 [br. m, 8 H, −NH*H*−], 2.93 [br. m, 8 H, −C*H*H−], 2.28 [br. m, 8 H, −CH*H*−], 1.47 (s, 12 H, −CH$_3$); (D$_2$O, room temp.): δ = 8.06 [AB$_2$, 3 lines, ^3J(HH) = 7.34/8.07 Hz, 2 H, H^4], 7.65 [AB$_2$, 2 lines, ^3J(HH) = 8.07 Hz, 4 H, H^{3,5}], 2.78 [d, ^2J(HH) = 12.47 Hz, 8 H, −C*H*H−], 2.38 [d, ^2J(HH) = 13.20 Hz, 8 H, −CH*H*−], 1.43 (s, 12 H, −CH$_3$). − ^{13}C NMR ([D$_6$]DMSO, room temp.): δ = 165.83 (s, C2/6), 140.39 (s, C4), 120.37 (s, C3/5), 47.09 (s, >C<), 44.96 (s, −CH$_2$−), 21.55 (s, −CH$_3$). − UV/Vis (water): λ max (ε) = 293 (19 707). − $C_{26}H_{50}Cl_4Co_2N_{10}O_2 \cdot 3H_2O$ (848.5): calcd. C 36.81, H 6.65, N 16.51; found C 37.01, H 6.58, N 16.79.

Procedure B: The preparation was carried out in air. To a mixture of **1**·4HCl (3.27 g, 8.23 mmol) and $Na_3[Co(CO_3)_3] \cdot 3H_2O$[74] (2.98 g, 8.23 mmol) was added a mixture of water and methanol (1:1, 100 mL) in one portion, which resulted in immediate foaming (evolution of CO_2). The mixture was heated at reflux until CO_2 evolution ceased. Upon standing at room temperature, a microcrys-

Table 4. Crystallographic data for compounds **5**, **7**, **12** and **13**

	5	**7**	**12**	**13**
Empirical formula	$C_{26}H_{62}Cl_2Co_2N_{10}O_{14}S_2$	$C_{26}H_{70}ClCo_2N_{10}O_{24}S_4$	$C_{13}H_{27}Br_2CoF_6N_5OP$	$C_{13}H_{31}BrCoN_5O_6S$
Formula weight	991.74	1188.47	633.12	524.33
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group (no.)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P2_1/m$ (no. 11)	$P\bar{1}$ (no. 2)
a [Å]	27.206(11)	9.859(2)	10.873(1)	8.227(2)
b [Å]	7.802(1)	9.940(2)	7.980(1)	9.891(2)
c [Å]	22.011(2)	13.437(2)	13.193(2)	13.595(2)
α [°]	90	72.83(1)	90	104.84(1)
β [°]	119.26(2)	89.03(2)	110.93(1)	94.23(1)
γ [°]	90	72.77(1)	90	100.16(1)
Z	4	1	2	2
V [Å^3]	4076(2)	1198.1(4)	1069.2(2)	1044.3(4)
$\rho_{calcd.}$ [g cm^{-3}]	1.616	1.647	1.967	1.667
Diffractometer	Siemens P4	Siemens P4	Siemens P4	Siemens P4
λ[Å][a]	0.71073	0.71073	0.71073	0.71073
Crystal size [mm^3]	$0.40 \times 0.40 \times 0.20$	$0.60 \times 0.40 \times 0.35$	$0.90 \times 0.38 \times 0.10$	$0.65 \times 0.50 \times 0.40$
T [°C]	293(2)	200(2)	295(2)	200(2)
Absorption correction	–	Psi-scan	Psi-scan	Psi-scan
T_{min}/T_{max}	–	0.653/0.945	0.018/0.064	0.072/0.138
Scan	ω	ω	ω	ω
2Θ range	$4 \leq 2\Theta \leq 54$	$4 \leq 2\Theta \leq 56$	$4 \leq 2\Theta \leq 54$	$4 \leq 2\Theta \leq 54$
Measured reflections	10137	6670	3290	5487
Unique reflections	4417	5685	2509	4524
Observed reflections[b]	2527	4732	1859	3405
μ(Mo-K_α) [mm^{-1}]	1.122	1.014	4.681	2.873
Refined parameters	253	409	158	347
Data/parameter ratio	17.5	13.9	15.9	13.0
$wR2$ (all data)[c]	0.1455	0.1232	0.1712	0.1256
$R1$ (obs. data)[d]	0.0560	0.0461	0.0601	0.0506
ρ_{fin}(max/min) [e Å^{-3}]	0.810/−0.873	0.766/−1.553	1.142/−1.657	0.836/-1.515
Weighting scheme[e]	$k = 0.0563/l = 0$	$k = 0.0708/l = 0.6384$	$k = 0.1093/l = 0.8048$	$k = 0.0715/l = 0.2747$

[a] Mo-K_α, graphite monochromator. – [b] With $F_o \geq 4\,\sigma(F)$. – [c] $wR2 = (\{\Sigma[w(F_o^2 - F_c^2)^2]\}/\{\Sigma[w(F_o^2)^2]\})^{0.5}$. – [d] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F > 4\sigma(F)$. – [e] $w = 1/[\sigma^2(F_o^2) + (k \cdot P)^2] + l \cdot P$ and $P = (F_o^2 + 2F_c^2)/3$.

talline green–brown material precipitated, leaving a reddish brown filtrate. The solid was collected by filtration, washed repeatedly with small volumes of methanol and dried in vacuo (0.61 g, 0.73 mmol, 17.7% relative to **1**). – IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1} (s), 3186s, 3094s, 2964w, 2938w, 2878w, 1605s, 1467s, 1394w, 1276w, 1206w, 1164m, 1102m, 1040m, 816w, 763m, 560w, 482w. – $C_{26}H_{50}Cl_4Co_2N_{10}O_2 \cdot 1.5H_2O \cdot 0.5CH_3OH$ (837.5): calcd. C 38.01, H 6.62, N 16.72; found C 38.32, H 7.03, N 17.12.

[(1)Co–O–O–Co(1)]Cl$_5$ (6): The filtrate obtained as under B above (100 mL) was acidified with hydrochloric acid (3 N, 5 mL), and stirred overnight at room temperature. A green precipitate formed which was collected by filtration, washed with small volumes of methanol, and dried in vacuo (0.69 g, 0.59 mmol, 14% relative to **1**). An anion exchange with NH_4PF_6 was carried out in order to obtain analytically pure material. – IR (KBr): $\tilde{\nu}$ = 3627 cm^{-1} (w), 3426w, 3083m, 1607m, 1472m, 1441w, 1220w, 1178w, 1112w, 1032w, 938vs, 764w, 740w, 559s. – ESR (DMSO, 120 K): $g = 2.0269$. – UV/Vis (water): λ max (ε) = 698 (1720), 464 (360), 307 (28940), 208 (42520). – $C_{26}H_{50}Cl_2Co_2F_{18}N_{10}O_2P_3 \cdot H_2O$ ([(**1**)Co–O–O–Co(**1**)] $Cl_2(PF_6)_3 \cdot H_2O$, 1176): calcd. C 26.55, H 4.46, N 11.91; found C 26.53, H 4.39, N 11.82.

[(1)CoCl]Cl$_2$ (4): The mother liquor obtained in the preparation of **6** (100 mL) was loaded on a Dowex 50WX2 cation exchange column (∅ 15 mm, length 250 mm). Gradient elution with HCl gave an orange–red fraction (3 N HCl, 300 mL). Reducing its volume to ca. 50 mL on a rotary evaporator induced precipitation of a microcrystalline pink solid, which was collected, washed with small volumes of an ethanol/diethyl ether mixture (1:1), and diethyl ether, and dried in vacuo (0.74 g, 1.6 mmol, 19.2% relative to **1**). – IR (KBr): $\tilde{\nu}$ = 3394 cm^{-1} (s), 3199s, 3086s, 2970w, 2882w, 1603s, 1470m, 1396w, 1289w, 1261w, 1214w, 1171m, 1104m, 1042m, 826w, 774w. – ^{1}H NMR ([D$_6$]DMSO, room temp.): δ = 8.19 [AB$_2$, 3 lines, ^3J(HH) = 7.66/7.90 Hz, 1 H, H^4], 7.69 [AB$_2$, 2 lines, ^3J(HH) = 7.90 Hz, 2 H, H^{3,5}], 6.46 [br. m, 4 H, –N*H*H–], 5.23 [br. m, 4 H, –NH*H*–], 2.74 [br. m, 4 H, –C*H*H–], 2.25 [br. m, 4 H, –CH*H*–], 1.47 (s, 6 H, –CH$_3$). – ^{13}C NMR ([D$_6$]DMSO, room temp.): δ = 165.18 (s, C2/6), 140.98 (s, C4), 121.00 (s, C3/5), 47.16 (s, >C<), 44.16 (s, –CH$_2$–), 21.33 (s, –CH$_3$). – $C_{13}H_{25}Cl_3CoN_5 \cdot 0.75C_2H_5OH \cdot H_2O$ (469.2): calcd. C 37.12, H 6.77, N 14.93; found C 37.49, H 7.04, N 15.27.

[(1)CoBr]Br$_2$ (9). – Procedure A: The preparation was carried out in air. To a mixture of **1**·4HBr·MeOH (6.07 g, 10.0 mmol) and $Na_3[Co(CO_3)_3] \cdot 3H_2O$ (3.62 g, 10.0 mmol) was added a mixture of water and methanol (50:50 v/v, 180 mL) in one portion, which resulted in immediate foaming. After CO_2 evolution had subsided, hydrobromic acid (1.0 N, 10 mL) was added. The mixture was heated at reflux until CO_2 evolution ceased. The mixture (still hot) was filtered to remove unchanged $Na_3[Co(CO_3)_3]$, and a brown crystalline material precipitated on standing at room temperature, leaving a reddish brown mother liquor. The solid was removed by filtration and washed with methanol ([(**1**)–Co–O–O–Co–(**1**)]$Br_4 \cdot 3H_2O$, 2.85 g, 55.5% relative to **1**). The filtrate was loaded on a Dowex 50WX2 cation exchange column (∅ 15 mm, length 250 mm). Gradient elution with HBr gave a red–violet fraction (3 N HBr, 300 mL). Reducing its volume to ca. 50 mL on a rotary evaporator induced precipitation of a microcrystalline purple solid, which was collected, washed with small volumes of an ethanol/diethyl ether mixture (50:50 v/v), and dried in vacuo (1.23 g, 2.24 mmol, 22.4% relative to **1**).

Procedure B: $[(\mathbf{1})\text{−Co−O−O−Co−}(\mathbf{1})]Br_4·3H_2O$ (0.30 g, 0.29 mmol) was suspended in hydrobromic acid (3 N, 25 mL) and stirred for one hour. Over this period the colour of the suspension changed from brown to green. The precipitate was collected by filtration, washed with small volumes of an ethanol/diethyl ether mixture (50:50 v/v) and dried in vacuo ($[(\mathbf{1})\text{−Co−O−O−Co−}(\mathbf{1})]Br_5$, 0.20 g, 65% relative to **1**), leaving a reddish violet filtrate. Reducing the volume of the filtrate to ca. 50 mL on a rotary evaporator induced precipitation of a microcrystalline reddish purple solid, which was collected, washed with a small amount of ethanol/diethyl ether (50:50 v/v) and dried in vacuo. As elemental analysis was not yet satisfactory, and in order to obtain single crystals suitable for X-ray crystallography, an anion exchange was carried out with NH_4PF_6. − IR (KBr): $\tilde{\nu}$ = 3671 cm^{-1} (m), 3596m, 3421w, 3304m, 3181m, 3088m, 2951w, 1595s, 1470m, 1400w, 1284w, 1210w, 1170m, 1104m, 1034m, 846vs, 741w, 559vs, 415w. − ^1H NMR ($[D_6]$DMSO, room temp.): δ = 8.21 [AB_2, 3 lines, $^3J(HH)$ = 7.90/7.66 Hz, 1 H, H^4], 7.71 [AB_2, 2 lines, $^3J(HH)$ = 7.93 Hz, 2 H, $H^{3,5}$], 5.40 [br. m, 8 H, $-NH_2$], 2.76 [br. m, 4 H, $-C\mathit{H}H-$], 2.26 [br. m, 4 H, $-CH\mathit{H}-$], 1.46 (s, 6 H, $-CH_3$). − ^{13}C NMR ($[D_6]$DMSO, room temp.): δ = 165.06 (s, C2/6), 141.11 (s, C4), 121.22 (s, C3/5), 46.77 (s, >C<), 44.12 (s, $-CH_2-$), 21.27 (s, $-CH_3$). − $C_{13}H_{25}Br_2CoF_6N_5P·H_2O$ ($[(\mathbf{1})CoBr]BrPF_6·H_2O$, 633.1): calcd. C 24.66, H 4.30, N 11.06; found C 24.86, H 4.00, N 11.09.

$[(\mathbf{1})CoSO_3]Br$ (13): Manipulations were performed under nitrogen in deoxygenated solvents using standard Schlenk techniques. To a mixture of $\mathbf{1}·4HBr·MeOH$ (0.61 g, 1.0 mmol) and $Na_3[Co(CO_3)_3]·3H_2O$ (0.36 g, 1.0 mmol) was added water (25 mL) in one portion (with stirring), which resulted in immediate foaming (evolution of CO_2). After CO_2 evolution had ceased, a solution of $Na_2S_2O_4$ (0.1 g, 0.5 mmol) and $NaHCO_3$ (0.17 g, 2.0 mmol) in water (10 mL) was added, and the mixture stirred overnight. Precipitated Co_2S_3 was removed by filtration, and the hydrogen sulfide which evolved after acidification identified by its smell. The volume of the mother liquor was reduced until an orange−brown precipitate appeared, and the suspension then kept at 4 °C overnight in order to complete precipitation. The microcrystalline material was collected by filtration, washed repeatedly with small volumes of ethanol and dried in vacuo (0.22 g, 39% relative to **1**). The volume of the mother liquor was reduced further, and storage at 4 °C produced a small batch of single crystals suitable for X-ray structural analysis. Anion exchange of the major fraction with NH_4PF_6 in dilute aqueous ammonia gave crystalline material which analysed correctly for C, H, and N, and was used for IR and NMR spectroscopic characterization. − IR (KBr): $\tilde{\nu}$ = 3471 cm^{-1} (s), 3329s, 3227s, 2975w, 2890w, 1670w, 1606m, 1471m, 1402w, 1283w, 1206w, 1109s, 1082s, 1025m, 984vs, 840vs, 770w, 740w, 638m, 558s, 510w. − ^1H NMR ($[D_6]$DMSO, room temp.): δ = 8.26 [AB_2, 3 lines, $^3J(HH)$ = 7.90/7.90 Hz, 1 H, H^4], 7.80 [AB_2, 2 lines, $^3J(HH)$ = 7.90 Hz, 2 H, $H^{3,5}$], 3.99 [br. m, 8 H, $-NH_2$], 2.65 [br. m, 4 H, $-C\mathit{H}H-$], 2.15 [br. m, 4 H, $-CH\mathit{H}-$], 1.40 [br. s, 6 H, $-CH_3$]. − ^{13}C NMR ($[D_6]$DMSO, room temp.): δ = 166.02 (s, C2/6), 140.24 (s, C4), 120.09 (s, C3/5), 45.29 (s, >C<), 44.34 (br. s, $-CH_2-$), 21.12 (s, $-CH_3$). − $C_{13}H_{25}CoF_6N_5O_3PS·2H_2O$ (571.4): calcd. C 27.33, H 5.12, N 12.26, S 5.61; found C 27.51, H 5.46, N 12.19, S 5.44.

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